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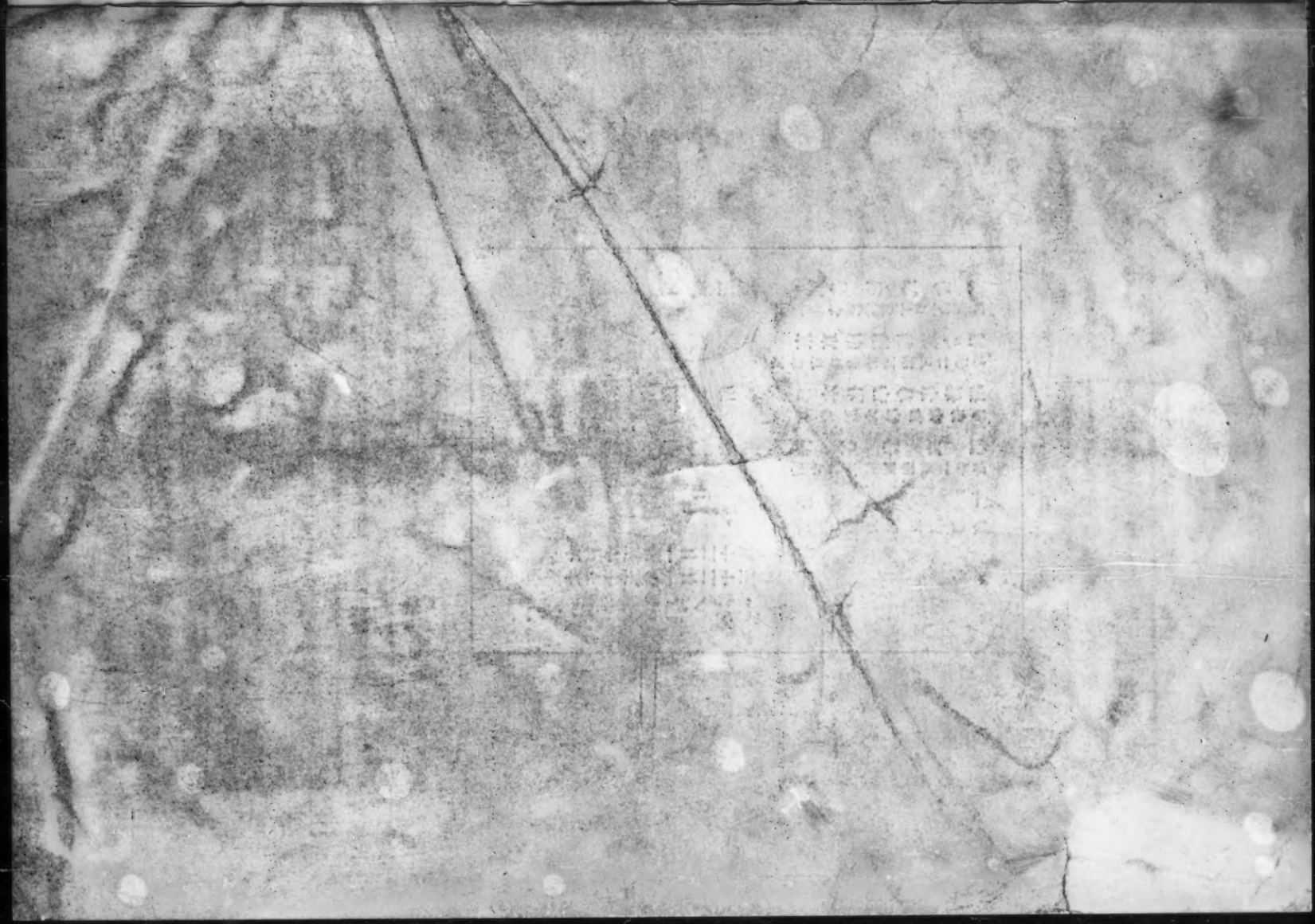


DEFLECTION OF A FLAME IN THE ELECTRIC FIELD.[1]

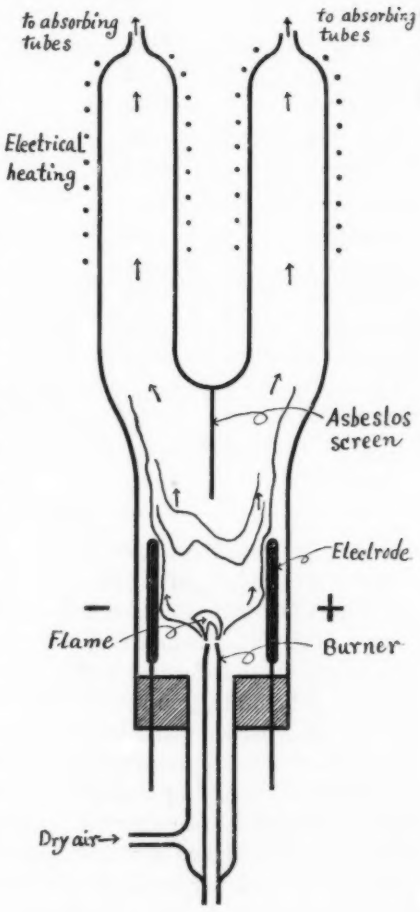
By Yuzaburo SHIBATA.

Received November 4, 1925. Published February 28, 1926.

It is well known that[2] a flame deflects itself when it is brought into an electric field. This fact can be explained as the result of the migration of the oppositely charged ions of a flame in different directions in an electric field. So we can catch differently charged particles in separate vessels and analyse them.

Ordinary Coal Gas Flame. If we put a small non-luminous flame of an ordinary coal gas burner in an electric field, the visible part of the flame is deflected towards the negative pole. But the flow of the hot gas produced by the flame streched itself almost symmetrically towards both electrodes. This fact can easily be observed by its shadow on a screen projected by strong illumination. The following experiment has been carried out to study the chemical compositions of the different parts obtained by electrical deflection.

A small ordinary coal gas flame is burnt in a two wayed glass cylinder as shown in the accompanying figure, the electric field being applied by a Wimshurst machine. Then the hot gases which was splitted by the field will go up



(1) Read before the Chemical Society of Japan, December 5, 1925.

(2) J. J. Thomson, Conduction of Electricity Through Gas. 1906, page 230.

separately along the two ways. By use of the tubes of calcium chloride and soda lime, the relative amounts of carbon dioxide and water were determined in each portions. The results are shown in the following table, together with the blank tests.

Electrode	Carbon dioxide	Water vapour	$\frac{CO_2}{H_2O}$	Ratio
	gr.	gr.		
Left (+)	0.494	0.341	1.45	1.02
Right (−)	0.615	0.415	1.48	
Left (+)	0.855	0.604	1.42	1.05
Right (−)	0.953	0.642	1.49	
Left (+)	0.519	0.375	1.39	1.02
Right (−)	0.560	0.396	1.42	
Left (−)	1.353	0.982	1.38	1.03
Right (+)	1.243	0.930	1.34	
Left (−)	0.825	0.551	1.50	1.04
Right (+)	0.553	0.385	1.44	
Left (−)	0.269	0.2095	1.28	1.04
Right (+)	0.177	0.143	1.24	
Left (no field)	0.2595	0.1675	1.55	1.00
Right (no field)	0.1865	0.1205	1.55	
Left (no field)	1.064	0.6375	1.67	1.00
Right (no field)	0.804	0.4825	1.67	

As seen from the above table, carbon dioxide is always in excess at the negative electrode than at the positive. The reason of this fact might be explained as follows. The molecules of a gas will split up into atoms or atomic groups in the intermediate stages of combustion, and some of the atoms or the atomic groups thus formed will be charged. It is probable that the carbon atom or the atomic groups CH, CH_2 CH_3 etc. have the positive charges, for the glowing carbon particles of a luminous flame in an electric field are strongly attracted to the negative electrode.

Flame Containing Sodium Chloride Vapour. In this case the sodium atom is supposed to be charged positively, and the chlorine atom negatively. This has been shown by the following experiment. When small silver plates are placed perpendicular to the electric field at a small distance from the flame at each side on the electrode, a purplish white deposit of silver chloride is seen on the surface of the silver plate on the side of the positive electrode, notwithstanding that the flame is deflected to the negative electrode as a whole.

Flame Containing Cupric Chloride. The flame has been obtained by blowing the ammoniacal solution of cupric chloride into the coal gas flame. In this case the copper atom is charged positively, and the chlorine atom negatively, which has been shown by a similar experiment as above. Reddish deposit of copper was seen at the negative electrode, while whitish deposit of silver chloride at the positive electrode.

The auther's thanks are due to Prof. Sameshima for his kind guidance.

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THE MOLECULAR ASSOCIATION OF PHENOL IN BENZENE AND WATER.

By **Kwantaro ENDO.**

Received November 29, 1925, Published February 28, 1926.

It has already been discussed by many investigators[1] that the partition coefficient of phenol between benzene and water is not constant but varies with its concentration, although the problem has not yet been solved. H. Hirobe[2] studied the partition of phenol between chlorobenzene and water, and reached the conclusion that in chlorobenzene there exists the chemical equilibrium,

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

while in water only the monomolecular phenol is present. As benzene is very similar in chemical natures to chlorobenzene, we may expect the same conclusion in the case of benzene. Following experiments were undertaken from this point of view.

I. Partition of Phenol between Benzene and Water at 25°C.

The measurements of the partition coefficient were carried out at 25° in the usual manner. Specially purified phenol and benzene were employed. Phenol was determined by the bromine method which was tested and found very satisfactory. The results are shown in Table 1, where W and B represent the molar concentrations of phenol calculated as C_6H_5OH in the aqueous and in the benzene layer respectively.

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(1) Rothmund and Wilsmore, *Zeit. physik. Chem.*, 40 (1902) 611.
W. Vaubel, *J. prakt. Chem.*, 67 (1903) 473.
James C. Philip and C.H. Douglas Clark, *J. Chem. Soc.* 127 (1925) 1274.

(2) H. Hirobe, *J. Coll. Science Imp. Univ. Tokyo*, 25 (1908) Art. 12.

TABLE 1.

Molar Concentrations of Phenol in		Partition Coeff.
Benzene Layer B	Aqueous Layer W	$P=\frac{W}{B}$
1.0442	0.2372	0.2272
0.7803	0.2052	0.2630
0.5437	0.1645	0.3026
0.2422	0.0934	0.3855
0.1177	0.0501	0.4256

Thus the values of P decrease with increasing concentration, as other investigators have already found.

At first, we assume that the following equilibrium is established in the benzene layer,

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

while only single molecules of phenol are present in the aqueous layer. Let c_1 and c_3 represent the molar concentrations in benzene of C_6H_5OH and $(C_6H_6O)_3$ respectively, then by the law of mass action,

$$Kc_1^3=c_3,$$

where K denotes the association constant. Moreover, there is the relation,

$$B=c_1+3c_3=c_1+3Kc_1^3.$$

Now by the law of partition the ratio of c_1 and W is to be constant; so

$$\gamma W=c_1$$

where γ is the real partition coefficient of C_6H_5OH between benzene and water.

Then, $B=\gamma W+3\gamma^3KW^3$ .....(1)

or $B/W=1/P=\gamma+3\gamma^3KW^2$ (2)

If we plot $1/P$ as ordinate and W^2 as abscissa, then we must obtain a straight line, providing our assumption is correct. Figure 1 which shows quite a straight line, has been drawn in such a manner. The equation (2), therefore, is correct and consequently our assumption is right.

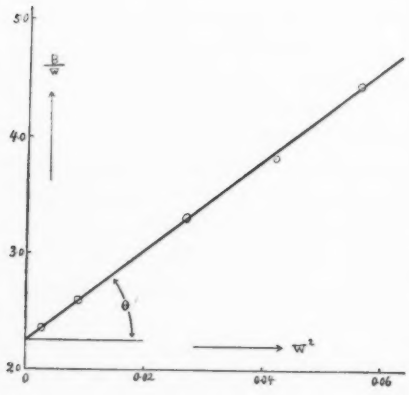

Fig. 1.

In the next place, we can find the values of γ and K from Fig. 1, thus

$$(1/P)_{W=0}=\gamma=2.25$$

and

$$\tan\theta=\frac{d(1/P)}{d(W^2)}=3\gamma^3K=37.77$$

I have calculated these values more exactly by the method of the least squares and obtained

$$3\gamma^3K=37.71 \quad \text{and} \quad \gamma=2.272$$

Then $K=1.072$.

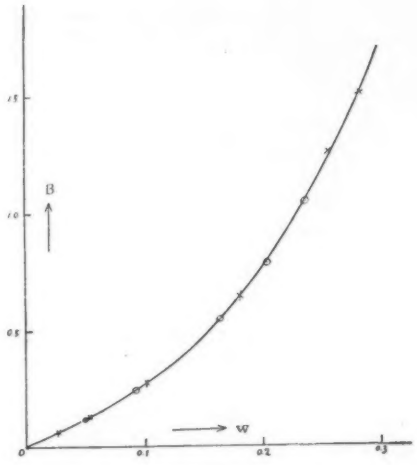

Fig. 2.

So the equation (1) becomes

$$B=2.272\,W+37.71\,W^3 \quad \cdots\cdots\cdots\cdots(3)$$

The curve in Fig. 2 has been drawn by the equation (3) and the circlets denote the points observed by the author, and the crosses by Rothmund and Wilsmore. The agreement between the theory and the experiment is quite satisfactory.

II. Depression of the Freezing Point of the Aqueous Phenol Solution.

The cryoscopic experiments were also done in order to determine the molecular states of phenol in water. The experiments were carried out on a larger scale than the ordinary cryoscopic method to get the greater accuracy. About 500 cc. of solution have been used each time. The results are shown in Table 2, where C denotes the molar concentration of phenol calculated as C_6H_5OH.

They are also shown graphically in Fig. 3, which represents a d–C curve. If the Raoult's law holds, d–C curve must be a straight line represented by the equation $d=kC$, ($k=1.86$). But as we see in Fig. 3, it is not a straight line, though the deviation is not large. It shows a regular downward deviation which suggests that there occurs an association of phenol

TABLE 2.

Weight of Water in gram w.	Weight of Phenol in gram g.	$C=\frac{1000g}{94.048w}$	Depression of Freez. Pt. in degree d.
499.4	18.8698	0.4016	0.676
499.4	14.2540	0.3034	0.524
499.4	10.7330	0.2284	0.407
499.3	8.4313	0.1795	0.325
499.4	5.7585	0.1226	0.228
499.4	4.0364	0.0859	0.165
499.4	2.6506	0.0564	0.110
499.3	2.4515	0.0522	0.101

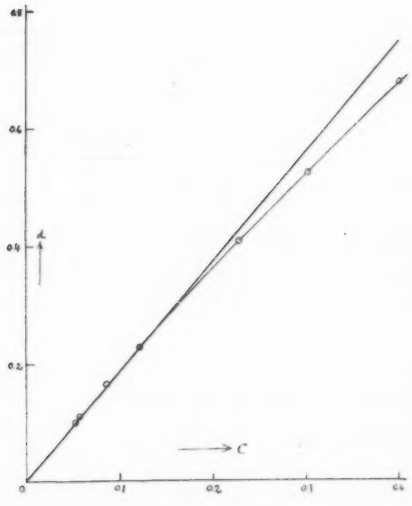

Fig. 3.

in a small degree in concentrated solutions. Generally, the degree of association decreases with the elevation of the temperature. So at 0°C. the association of phenol is perceptible when the molar concentration is greater than 0.2, while in more dilute solutions it can safely be assumed that there is no association as has been stated in the partition experiment.

Now we will assume

$$3C_6H_5OH \rightleftarrows (C_6H_6O)_3$$

in aqueous solution at 0°C. If c_1' and c_3' denote the molar concentrations of C_6H_5OH and $(C_6H_6O)_3$ respectively, then

$$K'c_1'^3=c_3',$$

where K' is the association constant of phenol in water. The analytical concentration C becomes

$$C=c_1'+3c_3',$$

and the depression of freezing point must be expressed by

$$d=k(c_1'+c_3').$$

Therefore, $$C-\frac{d}{k}=2c_3' \quad \text{or} \quad c_3'=\frac{1}{2}\left(C-\frac{d}{k}\right) \cdots\cdots (4)$$

and $$c_1' = \frac{d}{k} - c_3' \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

By using these two equations we can calculate c_1' and c_3' from Fig. 3 or directly from the observed data. We can also calculate the value of $K' = c_3'/c_1'^3$.

As we see in Fig. 3 the experimental points at concentrations lower than $C = 0.2$ almost coincide with the theoretical line of Raoult, so this part has been excluded from the calculation. The results are shown in Table 3.

TABLE 3.

C	d	d/k	c_3'	c_1'	K'
0.4000	0.673	0.3618	0.0191	0.3427	0.47
0.3500	0.596	0.3204	0.0148	0.3056	0.52
0.3000	0.519	0.2814	0.0093	0.2721	0.46
0.2500	0.441	0.2371	0.0065	0.2306	0.53
0.2000	0.359	0.1930	0.0035	0.1895	0.51
				Mean $K' = 0.50$	

The constancy of K' is satisfactory.

Summary.

1. From the measurement of the partition coefficient of phenol between benzene and water, it has been proved that phenol is in the state of chemical equilibrium

$$3C\,H_5OH \rightleftarrows (C_6H_6O)_3$$

in the benzene layer at 25°C.

2. From the measurement of the freezing point of the aqueous phenol solution, it has also been proved that phenol is in the chemical equilibrium similar to the above in the aqueous solution at 0°C.

It is to be emphasized that phenol associates itself in tripple molecules and not in double molecules.

My best thanks are due to Professor K. Ikeda for his kind guidance in the present experiments.

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THE HEATS OF FUSION OF SOME ORGANIC SOLVENTS WHOSE MELTING POINTS ARE RELATIVELY LOW.

By **Shinroku MITSUKURI.**

Received November 30, 1925. Published February 28, 1926.

The heats of fusion of organic solvents, whose melting points are relatively low, have scarcely been measured up to the present. O. Maass and L. J. Waldbauer[1] measured the heat capacities of several organic solvents between various points at low temperatures and at room temperature, and thence calculated their heats of fusion. E. Beckmann and his co-workers[2] measured the lowerings of freezing points of solutions in organic solvents and calculated the heats of fusion of those solvents by the van't Hoff's formula.

The present author also determined the lowerings of the freezing points of the solutions, and thence calculated the heats of fusion of several solvents by a thermodynamical formula. He, however, constructed an apparatus of new design, which was specially suitable for the determination of the melting points with a relatively small quantity of the samples.

I. The Apparatus and the Method of the Experiment.

The relation between the freezing point and the concentration of a solution is given by the following formula, which can be proved thermodynamically : that is,

$$\frac{d \ln N}{dT} = \frac{Q}{RT^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where N is the molar fraction of the solvent and Q is the heat of fusion of the solvent at the freezing point of the solution, T. Now, if the range of temperature is small and Q is taken as constant over this range, formula (1) can be integrated to the following :

$$\ln \frac{N}{N'} = \frac{Q}{R} \left\{ \frac{1}{T'} - \frac{1}{T} \right\} \quad \cdots\cdots\cdots\cdots\cdots (2)$$

where T and T' are the freezing points of the solutions with the concentrations N and N' respectively. By this formula, the heat of fusion of the

(1) Maass & Waldbauer, *J. Am. Chem. Soc.*, **47** (1925), 1.

(2) Beckmann & Waentig, *Z. anorg. allgem. Chem.*, **67** (1910), 17.
Beckmann & Faust, *Z. physik. Chem.*, **89** (1915), 249.

solvent can be calculated from the freezing points of two solutions at different concentrations.

It is general, however, that a pretty large quantity of the sample is necessary to determine the freezing points of organic solvents, because they are easy to supercool. The present author, therefore, cools the sample once down to the temperature where it perfectly solidifies, thence heats it up, and takes the point, where its melting finishes, as the temperature the same as the freezing point of the solution. Solid organic matters, however, are generally bad conductors of heat, and they can not be maintained at uniform temperature throughout all their parts during the heating, and consequently they can not melt at the same moment when they are heated. To overcome this difficulty, the present author designed the metal vessel shown in Fig. 1.

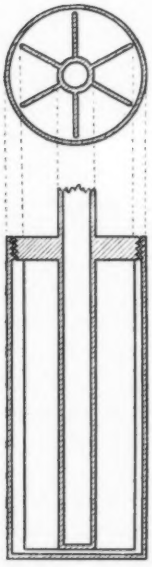

Fig. 1.

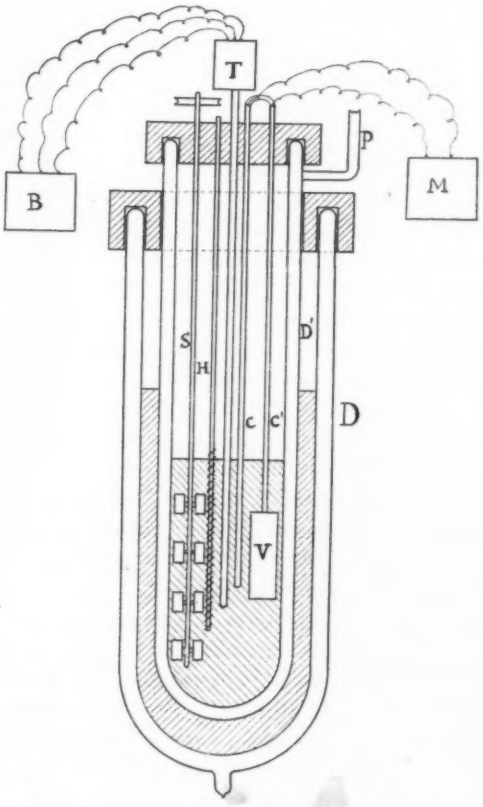

Fig. 2.

It consists of a cylindrical outer part and radial partition inside, whose function is to make heat conduction good so that the whole sample is maintained at the uniform temperature as far as possible. All the part of the vessel are made of brass, and the inner side is electrically coated with silver.

The whole apparatus is shown in Fig. 2. D is a large Dewar vessel, inside of which a double walled glass vessel D′ is placed ; the space between the double walls of this vessel is connected to a vacuum pump by the pipe P. V is the vessel for the sample shown in Fig. 1, in the middle hole of which one end of the thermocouple, C′, is inserted, the other end of it, C, is placed quite near to V. CC′ is an 8 series copper-constantan thermocouples, whose potential difference between C and C′ is measured by a millivoltmeter with 1/10 millivolt scale, M, and whose E.M.F. is 0.24 m.v. per degree centigrade. T is a platinum-resistance thermometer of about 2.5 ohms at 0°C., the resistance of which is measured by the bridge B, made by Leeds & Northrup Co, specially for the use with a resistance thermometer. By uniting these two the temperature can be measured with the precision of 1/100 degree centigrade. Inside the vessel D′, ether or pentane is put in, and this is stirred with the stirrer S to maintain a uniform temperature. H is a heater made of a coil of resistance wire, which is used for heating the liquid electrically.

The sample is put in the vessel V, the cover screwed in, sealed with water-glass, and then the vessel is placed in the liquid in D′. The space between the double walls of D′ is then filled with air to make heat conduction from the outside to the inside of the vessel good, and then liquid air is poured into D to cool the inside of D′. When the temperature of the liquid is about 20° below the point where the sample perfectly solidifies,—this is indicated by the cooling curve,—the vessel D is lowered so that D′ is out of the liquid air. Adjusting the electric current in the heater H and the degree of vacuum within the double walls, the heating rate inside D′ is regulated optionally. In this experiment the rate of 1.0—1.3 degree/minute is used. The temperature of the liquid in D′, which is measured by the thermometer T, is taken on abscissa and the E.M.F. of the thermocouple CC′, which corresponds to the temperature difference between the outside and the inside of V, is taken on ordinate, a curve is obtained. As the heat is absorbed at the region where fusion takes place, the temperature difference indicated by ordinate increases, and the curve ascending in this part, and when the heat absorption ends, the temperature difference again decreases and the curve descends ; thus it shows a maximum. The temperature where the extensions of the curve before and after the maximum intersect, minus the temperature difference corresponds to the maximum of the curve, is taken as temperature where fusion ends, that is the freezing point. Of course, this temperature may not indicate the true freezing point, but as the quantity which is needed

is not the absolute values of the temperature, but the difference of the temperatures, no correction on this deviation is necessary.

II. The Results of the Experiment.

The materials used were all specially purified in this laboratory from the pure chemicals of Kahlbaum.

The results are tabulated in the following tables.

Solvent	Solute	Mol. % 100 N.	Melt. pt. T.	$\frac{1}{T}$	log N
Chloroform	—	100.00	211.59	0.004726	0.0000
	Toluene	97.73	211.09	0.004739	− 0.0100
	Acetone	96.78	210.50	0.004750	− 0.0142
	Toluene	95.13	210.00	0.004762	− 0.0217
	Ether	94.08	209.31	0.004777	− 0.0265
	Acetone	90.80	207.91	0.004810	− 0.0419
Acetone	—	100.00	179.37	0.005575	0.0000
	Toluene	98.28	178.67	0.005597	− 0.0075
	Toluene	97.66	178.19	0.005612	− 0.0103
	Toluene	94.18	176.51	0.005665	− 0.0260
	Ether	92.88	175.73	0.005691	− 0.0321
Carbon-bisulphide	—	100.00	162.30	0.006161	0.0000
	Toluene	98.35	161.02	0.006211	− 0.0072
	Toluene	97.43	160.33	0.006237	− 0.0113
	Toluene	93.93	157.30	0.006357	− 0.0272
Ethyl-ether	—	100.00	150.61	0.006640	0.0000
	Acetone	98.78	150.41	0.006650	− 0.0053
	Acetone	97.37	149.53	0.006688	− 0.0116
	CS_2	96.15	149.53	0.006688	− 0.0170
	Methyl-alc.	95.86	149.34	0.006696	− 0.0184
	Acetone	95.12	148.85	0.006718	− 0.0217
Methyl-alcohol	—	100.00	177.40	0.005637	0.0000
	Ether	98.92	176.17	0.005676	− 0.0047
	Toluene	96.84	173.81	0.005753	− 0.0139
	Acetone	96.62	173.52	0.005763	− 0.0148
	Toluene	95.96	173.13	0.005776	− 0.0179
Ethyl-alcohol	—	100.00	157.93	0.006332	0.0000
	CS_2	99.11	157.25	0.006359	− 0.0039
	Methyl-alc.	97.83	156.37	0.006395	− 0.0094
	Methyl-alc.	97.04	155.59	0.006427	− 0.0131

If the formula (2) holds in the solutions investigated, the points on the diagrams in which $\log N$ and $\frac{1}{T}$ are taken as co-ordinates are to be on straight lines for each solvent. As the values in the above table nearly satisfy this condition, the heats of fusion of the solvents can be calculated by the formula from the values of two points on these straight lines. The results of the calculations are as follows:

Solvent.	Heat of fusion.
Chloroform	2080 calories.
Acetone	1300
Carbon-bisulphide	660
Ethyl-ether	1400
Methyl-alcohol	600
Ethyl-alcohol	650

The heat of fusion of chloroform was given by Beckmann and Faust as 2100 cal., which coincides with that of ours.

The heats of fusion of acetone and methyl-alcohol were given by Maass and Waldbauer as 1140 cal. and 520 cal., respectively, which are smaller than those of ours, but perhaps it is better to say that they concide with each other within experimental errors.

The heat of fusion of ethyl-ether was given by Beckmann and Waentig as 2030 cal. which is much larger than that of ours.

Summary.

An apparatus which is suited to determine the lowering of freezing point of organic solvents was described.

The lowerings of the freezing points of the solutions of chloroform, acetone, carbon-bisulphide, ethyl-ether, methyl-alcohol and ethyl-alcohol were determined, and their heats of fusion were calculated.

This paper is a brief abstract of the following papers:

The heats of fusion of chloroform, acetone and carbon-bisulphide. by S. Mitsukuri and S. Aoki.

The heats of fusion of ethyl-ether, methyl-alcohol and ethyl-alcohol. by S. Mitsukuri and K. Hara.

which are going to be published in the Science Reports of the Tohoku Imperial University. The full description of the experiments and some discussions on the results are to be found in the above papers.

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CATALYTIC ACTION OF REDUCED COPPER ON OXIMES (ON BECKMANN'S REARRANGEMENT, XV.)

By Shozo YAMAGUCHI.

Received December 18 1925. Published February 28 1926.

In the previous article[1] on this subject, the writer has stated that benzaldoximes when passed on reduced copper heated at 200° in an atmosphere of hydrogen were transformed into benzamide, benzonitrile and benzoic acid. The same experiment was extended to some aldoxime and ketoximes to draw some general conclusion from the experimental results, which might have an intimate connection with the explanation for the mechanism of Beckmann's rearrangement.

I. Furfuraldoxime.

20 gr. of the oxime, m.p. 89°, prepared according to the directions suggested by H. Goldschidt and E. Zanoli[2], were passed with hydrogen on reduced copper heated to 200°, and 2.8 gr. of solid and 4.5 gr. of liquid reaction products were obtained.

(A) Pyromusic Acid Amide.

The solid reaction product described above, was washed well with absolute ether, and then the amide, insoluble in ether, was recrystallised from hot alcohol in white beautiful crystals which melted at 141°–142°. The yield was 1.2 gr. It shows a blue colour, when treated with bromine water and caustic soda solution, as was mentioned by Saunders,[3] which on standing, changed to violet and then to red.

On analysis, it gave the following results :

0.1121 gr. subst. gave 0.2225 gr. CO_2 and 0.0528 gr. H_2O
0.1276 gr. subst. gave 14.6 c.c. N_2 at 23.5° and 750.2 mm.

Found :	C=54.13	H=5.27	N=12.81
Calc. for $C_5H_5O_2N$:	C=54.04	H=5.54	N=12.60

The compound seems, so far as studied, to be identical with pyromusic acid amide. For the confirmation, it was converted into the bromoderivative following the direction given by Saunders, and this substance melted at about 125° with decomposition, and gave the following analytical results :

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Uni., A,* 9 (1925) 33.
(2) *Ber. D. Chem. Ges.,* 25 (1892) 2573.
(3) *Am. Chem. J.,* 15 (1893) 135.

0.2416 gr. subst. gave 0.4183 gr. AgBr.

Found : Br=73.68

Calc. for $C_5H_5O_2NBr_4$: Br=74.21

(B) The Acidic and the Basic Substances.

The liquid reaction product (4.5 gr.) was combined together with the ether washing of the solid reaction product, and dry ammonia gas was passed into the mixed solution to isolate the acidic substance, when a small quantity of the ammonium salt of an acid was separated, but further study of its chemical nature was not possible owing to the modicum of the sample. The ethereal solution separated by filtration from the ammonium salt, was evaporated to dryness to get rid off the solvent, and the residue was treated with a mixture of ether and hydrochloric acid solution to separate the neutral substance from the basic one. To the acid solution a platinum chloride solution was added and a platinum double salt was obtained.

(C) The Neutral Substance.

From the neutral ethereal solution separated from the acidic solution, furfural was isolated in the usual way, and confirmed to be so from its boiling point and the colour reaction.

II. Benzamidoxime[1].

4.5 gr. of the oxime, m.p. 76°–77°, were passed on reduced copper heated to 200° in an atmosphere of hydrogen, and 1.9 gr. of solid and 1.3 gr. of liquid reaction products were obtained.

(A) Benzamide.

It was isolated, in white crystals, m.p. 126°, from the solid reaction product, by treating it with absolute ether and then dilute alcohol. The yield was 1.2 gr. It was analysed and the following results were obtained :

0.1188 gr. subst. gave 0.2991 gr. CO_2 and 0.0638 gr. H_2O.

0.1312 gr. subst. gave 0.15016 gr. N_2 (by Kjeldahl's Method).

Found : C=68.62 H=6.009 N=11.43

Cal. for C_7H_7ON : C=69.39 H=5.82 N=11.57

(B) The Acidic and the Basic Substances.

The liquid reaction product and the ethereal washing of the solid reaction product were combined together, and an acidic, basic and a neutral substances were isolated from the mixed solution by treating with dry ammonia gas, and then with hydrochloric acid successively. The acidic substance which separated in the form of an ammonium salt, amounting to 0.4 gr., was identified to be benzoic acid from its melting point (121°) and from other chemical properties, after the salt was converted into a free acid and purified.

(1) Tiemann, *Ber. D. Chem. Ges.*, 17 (1884) 128.

The basic substance was found to consist of a modicum of the reaction product.

(C) The Neutral Substance.

The neutral reaction product obtained in a liquid state, amounted to 0.6 gr., and was confirmed to be composed mostly of benzonitrile by subjecting it to reduction with metallic sodium and alcohol, and a trace of a basic substance was detected in the product.

III. Cinnamylaldoxime.

The oxime used in this experiment was prepared, according to the direction given by O. Brady and C. Thomas[1], from 20 gr. of cinnamylaldehyde, b.p. 125°–138°, 12 mm., and 15 gr. of hydroxylamine hydrochloride, and purified by crystallisation from benzene. It melted at 126°, and its yield was 16 gr.

16 gr. of the oxime were passed with pure hydrogen on finely divided copper heated at 200°, and obtained a tar-like substance and 6.8 gr. of a liquid reaction product. In order to isolate the acidic substance from the reaction product, dry ammonia gas was passed into its ethereal solution, but no precipitate appeared. It was then treated with hydrochloric acid to separate the basic substance from the neutral one.

The neutral substance was isolated in an oily form from the hydrochloric acid solution by extracting it with ether as usual. The yield was 1.1 gr. On standing it for a few days some crystals were separated from the oily matter, and it was confirmed that this was composed of cinnamic acid from its melting point of 132°–133°, and from its reaction. The oily residue separated from cinnamic acid was supposed, from the analogy of other cases, to be a mixture of cinnamyl aldehyde and the nitrile, but their presence could not be confirmed owing to the small amount of these substances (0.1 gr.)

Lastly, a resinous matter which remained with the copper in a reaction tube, was regarded as being formed by polymerisation of the reaction products mentioned above, though the chemical test for its confirmation was lacking.

IV. Di-benzyl Ketoxime.

8 gr. of di-benzyl ketoxime[2] which melted at 119°-120° were passed with hydrogen over reduced copper at 200°, and 1.9 gr. of pasty substance and 1.1 gr. of liquid were obtained. The former was treated with absolute ether and then recrystallised from hot water, and colourless crystals which

(1) *J. Chem. Soc.*, 121 (1922) 2103.

(2) *Ber. D. Chem. Ges.*, 21 (1888) 1316.

melted at 155° were obtained. The yield was 0.2 gr.

0.0919 gr. subst. gave 0.00958 gr. N_2 (by Kjeldahl's method).

Found : N=10.42, Calc. for C_8H_9NO : N=10.37.

The chemical properties and the analytical results agree well with those of phenylacetamide. The oily reaction product and the ether washing of the solid one were combined together, and acidic and neutral substances were isolated as usual.

The acidic substance was separated from the reaction product mentioned above, by means of ammonia in the form of an ammonium salt, then decomposed into free acid by means of hydrochloric acid, and was identified as phenylacetic acid from its melting point 76°–77°.

The neutral substance amounting to 2.6 gr. was subjected to distillation under 757 mm. and the following fractions were obtained :

Fraction	85°–120°	120°–130°	residue.
Yield	0.8 gr.	1.2 gr.	trace.

The second fraction was composed of liquid and solid substances, and the latter was separated by filtration, the liquid was supposed to be a mixture of 92% di-benzyl ketone and 8% benzyl nitrile by the nitrogen determination.

0.1205 gr. of the mixture gave 0.00154 gr. N_2 by Kjeldahl's method, whence it contains 0.00116 gr. of the nitrile. The existence of the ketone was confirmed by oximiration with hydroxylamine.

V. Benzophenone oxime.

14 gr. of the oxime were passed on reduced copper at 200° in an atmosphere of hydrogen, and 6.8 gr. of a liquid, and 0.3 gr. of a pasty substance were obtained.

From these reaction products trace of both acidic and basic substances could be isolated, but further confirmation of them was lacking owing to the small yield of the materials.

The neutral substance composed the larger part of the reaction products, and from this a crystalline substance was isolated through an alcohol solution, which melted at 202°–205°. The yield was 0.2 grm. It was soluble in hot benzene and chloroform. On analysis, it gave the following results :

0.1233 gr. subst. gave 0.4206 gr. CO_2 and 0.0765 gr. H_2O.

Found :	C=93.03	H=6.94
Calc. for. $C_{26}H_{22}$:	C=93.36	H=6.65

It was, thus, supposed to be a substance identical with tetraphenylethane.

To the alcoholic solution separated from the hydrocarbon, 4 gr. of hydroxy-

lamine hydrochloride and 6 gr. of caustic soda were added to separate some benzophenone, and the mixture was left to stand for 4 hours, and then the solvent was distilled off from the reaction products. 2.2 gr. of benzophenone oxime and a hydrocarbon were obtained.

The latter substance amounting to 4 gr., boiled at 135°–140°, 10 mm., melted at 27°. On analysis, it gave the following results:

0.1583 gr. subst. gave 0.5367 gr. CO_2 and 0.0930 gr. H_2O.

Found:	C = 92.47	H = 6.57
Calc. for. $C_{13}H_{12}$:	C = 92.81	H = 7.19

It was, thus, confirmed to be diphenyl methane.

In another experiment, 20 gr. of benzophenone oxime were passed with pure hydrogen over reduced copper heated at 200°, and 10 gr. of a liquid reaction product was obtained in a receiver cooled below 0° with a freezing mixture, and the product was immediately treated with absolute ether. To the ethereal solution dry hydrochloric acid gas, after drying with anhydrous sodium salphate, was passed, whereas hydrochloride was separated, filtered, and washed well with absolute ether. The hydrochloride, thus obtained, amounting to 0.5 gr. was supposed to be a mixture of the hydrochlorides of amine, ketimine and ammonia, and the hydrochloride of diphenylketimine was separated from the other constituents and purified by the method of Hantzsch and Kraft[1]. The yield was 0.1 gr.

The physical and chemical properties of the hydrochloride agreed well with those of the ketimine hydrochloride described already by Mignonac[2] and Lachmann[3].

Lastly, 1.0 gr. of benzophenone, 1.0 gr. of tetraphenylethane and 1.3 gr. of diphenyl methane were actually isolated from the residue separated from the diphenylketimine by means of hydrochloric acid.

VI. Acetonoxime.

20 gr. of the oxime and hydrogen were passed on reduced copper at 200° and 15 gr. of a liquid reaction product was obtained in a receiver cooled with a freezing mixture.

The reaction product was subjected to distillation on a water bath and the distillate boiling below 84° was collected. The distillate amounting to 12 gr. was treated with ether in an acidic solution to separate a basic from a neutral sabstance. From the ether solution, the solvent was evaporated off, and acetone was separated by means of sodium bisulphite. The yield was 3 gr.

The acid solution separated from the ether solution, was evaporated to

(1) *Ber. D. Chem. Ges.*, **24** (1891) 3516.
(2) *Comp. rend.*, **170** (1920) 936.
(3) *J. Am. Chem. Soc.*, **46** (1924) 1477.

dryness, and by treating it with chloroform an amine hydrochloride was separated from ammonium chloride by the difference of their solubilities in the solvent.

The amine hydrochloride, amounting to 1.5 gr., was analysed after being transformed into the double salt of platinum.

0.1778 gr. subst. gave 0.0655 gr. Pt. on ignition.

Found : Pt=36.84

Calc. for. $(C_3H_8NH_2 \cdot HCl)_2$ Pt Cl_4 : Pt=36.96

From the analytical result and the carbylamine test, the basic substance was confirmed to be isopropyl amine. The occurrence of a secondary amine in the reaction product was confirmed by further reactions.

A small amount of the oxime which escaped from the reaction together with some substance of disagreeable odour and of unknown chemical nature, was isolated from the residue in a distillation flask.

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